

Atmospheric Chemistry of 1-Octene, 1-Decene, and Cyclohexene: Gas-Phase Carbonyl and Peroxyacyl Nitrate Products

ERIC GROSJEAN,[†]
DANIEL GROSJEAN,^{*,†} AND
JOHN H. SEINFELD[‡]

DGA, Inc., 4526 Telephone Road, Suite 205,
Ventura, California 93003, and Department of Chemical
Engineering and Division of Engineering and Applied Science,
California Institute of Technology, Pasadena, California 91125

Atmospheric reactions of 1-octene, 1-decene, and cyclohexene have been studied in laboratory experiments involving alkene-ozone mixtures in the dark and alkene-NO and aldehyde-NO mixtures in sunlight. Major carbonyl products of the alkene-ozone reaction (with sufficient cyclohexane added to scavenge OH) were heptanal from 1-octene, nonanal from 1-decene, formaldehyde from both, and pentanal from cyclohexene. For 1-octene and 1-decene, carbonyl formation yields were consistent with the simple mechanism: $\text{RCH}=\text{CH}_2 + \text{O}_3 \rightarrow 0.5(\text{HCHO} + \text{RCHO}) + 0.5(\text{RCHO} + \text{H}_2\text{COO})$. Other carbonyls were formed and accounted for ca. 0.10–0.20 of the subsequent reactions of the RCHO biradical. Pentanal accounted for ca. 0.16 of the cyclohexene- O_3 reaction. Sunlight irradiation of alkene-NO and aldehyde-NO mixtures leads to carbonyls, alkyl nitrates, and peroxyacyl nitrates. Major carbonyl products of the OH-alkene reaction were heptanal from 1-octene, nonanal from 1-decene, and formaldehyde from both. Experimental data indicated that addition is an important pathway of the overall OH-1-alkene reaction, decomposition is important for the β -hydroxyalkoxy radicals that form following OH addition, and reaction with O_2 is of some importance for the alkoxy radicals that form in several pathways in the alkene-NO (sunlight), aldehyde-NO (sunlight), and peroxyacyl nitrate-NO (dark) systems. The extent of isomerization of alkoxy and β -hydroxyalkoxy radicals could not be assessed. Several peroxyacyl nitrates [$\text{RC}(\text{O})\text{OONO}_2$] were formed including those with $\text{R} = n\text{-C}_4\text{H}_9$ from cyclohexene, $\text{R} = n\text{-C}_5\text{H}_{11}$ from hexanal, and $\text{R} = n\text{-C}_6\text{H}_{13}$ from heptanal and from 1-octene. The thermal decomposition rates of $n\text{-C}_5\text{H}_{11}\text{C}(\text{O})\text{OONO}_2$ and $n\text{-C}_6\text{H}_{13}\text{C}(\text{O})\text{OONO}_2$, which were synthesized in the liquid phase and were characterized in a number of tests using electron capture gas chromatography,

were (in units of 10^{-4} s^{-1}) 0.72–2.02 ($T = 291\text{--}299 \text{ K}$) and 0.61–1.19 ($T = 291\text{--}295 \text{ K}$), respectively, at $p = 1 \text{ atm}$ of air. Comparison with data for lower molecular weight homologues including PAN ($\text{R} = \text{CH}_3$) suggests that the thermal stability of peroxyacyl nitrates may increase with the size of the n -alkyl substituent. The atmospheric persistence of the atmospheric oxidation products of 1-octene, 1-decene, and cyclohexene is briefly discussed.

Introduction

Olefins continue to receive considerable attention for their important role in atmospheric chemistry, and they contribute to the formation of ozone, other photochemical oxidants, and free radicals (1–3). Higher molecular weight (MW) olefins also contribute to the formation of aerosols (4–6). The atmospheric chemistry of olefins involves their reactions with ozone, the hydroxyl radical, and the nitrate radical. These reactions have been extensively studied in the case of the low molecular weight alkenes (7, 8). Less is known regarding the atmospheric chemistry of higher MW olefins and cyclic olefins. Cyclic olefins have been studied as precursors to dicarboxylic acids and to other secondary organic aerosols (1, 4–6, 9) and as simple structural homologues of an important category of biogenic hydrocarbons, the terpenes (10–12). Long-chain alkenes, up to 1-dodecene, have been investigated as aerosol precursors (12). Little information is available regarding their gas-phase reaction products.

In this work, we have investigated the atmospheric chemistry of three higher molecular weight olefins: 1-octene, 1-decene, and cyclohexene. The reaction of these olefins with ozone has been studied under conditions that minimize the role of OH (i.e., the reactions of OH with the alkenes and with the carbonyl products of the ozone-alkene reactions), thus enabling us to obtain unambiguous information on the nature and yields of the carbonyl products (13, 14). The oxidation of these olefins in the presence of nitric oxide in sunlight has been studied with focus on carbonyl products (from the olefin-OH reaction before the NO- NO_2 crossover, and from both ozone and OH reactions afterward) and on the formation of peroxyacyl nitrates [$\text{RC}(\text{O})\text{OONO}_2$]. We have documented the formation of peroxyacyl nitrates including $n\text{-C}_6\text{H}_{13}\text{C}(\text{O})\text{OONO}_2$. This high molecular weight peroxyacyl nitrate, not previously described, has been synthesized and has been characterized in a number of tests including its thermal decomposition. The relevant reaction mechanisms are outlined.

Experimental Methods

Cyclohexene (stated purity >99%, contains 0.01% BTH), 1-octene (98%, contains 2% unspecified isooctenes), 1-decene (94%, contains $\leq 2\%$ each of decane, 2-ethyl-1-

* Corresponding author telephone: (805) 644-0125; fax (805) 644-0142.

[†] DGA Inc.

[‡] California Institute of Technology.

octene, and 2-butyl-1-hexene), cyclohexane (>99.9%), hexanal (98%), heptanal, (99%), hexanoic acid anhydride (95%), and heptanoic acid anhydride (95%) were obtained from Aldrich Chemical Co. and were used without further purification. Experimental protocols employed in this study have been described in detail previously (10, 11, 14–21), and only brief summaries are given below.

Ozone–Alkene Reaction in the Dark. Mixtures of alkene and ozone were allowed to react in the dark and under ambient conditions ($p = 1$ atm of purified air, $T =$ room temperature, $RH = 55 \pm 10\%$) in the presence of 400 ppm of cyclohexane added to scavenge OH. The experiments were carried out in 3.7 and 3.9 m³ FEP Teflon film chambers covered with black plastic. The concentration of ozone was monitored by ultraviolet photometry using a calibrated continuous ozone analyzer (Dasibi Model 1108). The precision of the ozone measurements in the concentration range relevant to this study was ± 1 –2 ppb. Control experiments involving ozone, ozone–cyclohexane mixtures, and carbonyls in purified air were carried out as previously described (22, 23).

Sunlight Irradiation of Alkene–NO and Aldehyde–NO Mixtures. Mixtures of 1-octene, 1-decene, or cyclohexene (1.5–5.5 ppm) and nitric oxide (0.05–0.84 ppm) were allowed to react in sunlight in 3.7 m³ all-Teflon chambers. Sunlight irradiations were carried out in purified, humid air ($RH = 55 \pm 10\%$) at ambient temperature and atmospheric pressure. Oxides of nitrogen were measured by chemiluminescence using a Monitor Labs 8840 continuous analyzer calibrated using the diluted outputs of a certified cylinder of NO in N₂ and of a certified NO₂ permeation tube. Ozone was measured by ultraviolet photometry. The same protocol was employed to carry out sunlight irradiations of mixtures of nitric oxide with the aldehydes hexanal and heptanal in humid air ($RH = 55 \pm 10\%$) and in dry air (Liquid Air, “instrument dry air” grade, H₂O < 3 ppm, hydrocarbons < 0.1 ppm).

Measurements of Peroxyacyl Nitrates. Peroxyacyl nitrates were measured by electron capture gas chromatography using SRI 8610 gas chromatographs with Valco 140 BN detectors (15–18). Calibrations were carried out as described previously (15–18). Low molecular weight peroxyacyl nitrates including PAN were measured using a 70 cm long Carbowax column as described previously (15–18). Higher molecular weight peroxyacyl nitrates were measured using an identical but shorter (15 cm) column. Figure 1 summarizes retention time versus carbon number data for the C₂–C₇ *n*-alkyl-substituted peroxyacyl nitrates on the 15 and 70 cm columns employed in this study. Data for C₁–C₆ *n*-alkyl nitrates are also shown for comparison.

Several tests were carried out to confirm the presence of peroxyacyl nitrates. A tube heated to 180 °C, at which temperature peroxyacyl nitrates decompose (16–18), was inserted in the sampling line upstream of the gas chromatograph. This resulted in a near-complete (>90%) disappearance of the peaks assigned to peroxyacyl nitrates. Additional tests included the decomposition of peroxyacyl nitrates to alkyl nitrates in the liquid phase (see below) and their thermal decomposition in the gas phase in the presence of nitric oxide (see the following section).

Synthesis of Peroxyacyl Nitrates in the Liquid Phase. The preparation of C₁–C₄-substituted peroxyacyl nitrates has been described previously (16–18). In this work, the same method was extended to the synthesis of the higher molecular weight compounds, *n*-C₅H₁₁C(O)OONO₂ and

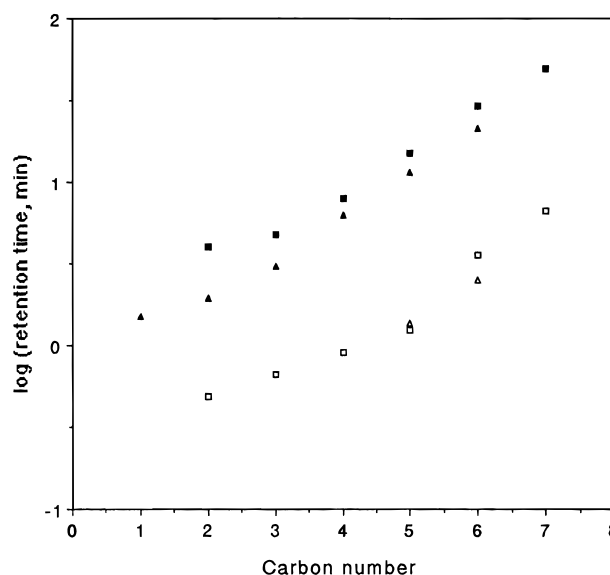
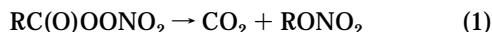


FIGURE 1. Retention times versus carbon number for C₂–C₇ *n*-alkyl-substituted peroxyacyl nitrates (squares) and for C₁–C₆ *n*-alkyl nitrates (triangles) on a 70-cm column (filled symbols) and on a 15-cm column (open symbols).

n-C₆H₁₃C(O)OONO₂. The method involved oxidation of the commercially available anhydrides to the corresponding peroxycarboxylic acids followed by nitration of the peroxycarboxylic acid by nitric acid (16–18). Solutions of *n*-C₅H₁₁C(O)OONO₂ and *n*-C₆H₁₃C(O)OONO₂ in *n*-dodecane (Aldrich, purity >99%) were stored at –5 °C in the dark. Aliquots of these solutions were allowed to stand at room temperature, where peroxyacyl nitrates decompose to yield the corresponding alkyl nitrates (16–18):



Aliquots of the solutions were injected in the Teflon chamber containing purified air, and the remaining peroxyacyl nitrate, if any, and the corresponding alkyl nitrate were measured by electron capture gas chromatography as described above.

Peroxyacyl Nitrate Thermal Decomposition Experiments. The thermal decomposition of peroxyacyl nitrates was studied as described previously by adding 5–10 ppm of nitric oxide to ppb levels of peroxyacyl nitrates in air. The peroxyacyl nitrates were present either in purified air or as reaction products in aldehyde–NO sunlight irradiation experiments. The thermal decomposition experiments were carried out in the dark at $T = 291$ – 299 K and $p = 1$ atm of air.

Chamber wall loss rates were measured in control experiments with ppb levels of PAN and PPN in purified air (no NO present). Loss rates measured in these experiments (duration = 6 h) were $(1.44 \pm 0.02) \times 10^{-6} \text{ s}^{-1}$ for PAN and $(1.15 \pm 0.03) \times 10^{-6} \text{ s}^{-1}$ for PPN, consistent with previous work (16–18). These loss rates are ca. 2 orders of magnitude smaller than those measured in the peroxyacyl nitrates thermal decomposition experiments.

Carbonyl Sampling and Analysis. Carbonyl samples were collected by drawing air through C₁₈ cartridges coated with acidic 2,4-dinitrophenylhydrazine (DNPH). The air flow rate was 0.77 L/min, and the sampling duration was 30 or 60 min. Collocated cartridges (to assess precision), sampling trains with two cartridges in series (to verify absence of breakthrough), and cartridge blanks were

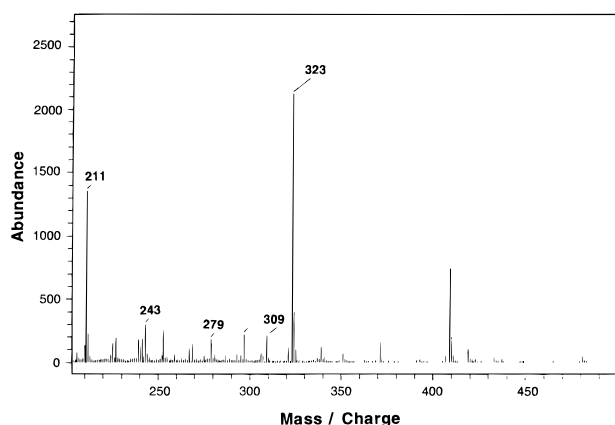


FIGURE 2. Chemical ionization mass spectrum of a sample collected in one of the 1-decene–ozone–cyclohexane experiments. Major peaks in the spectrum include the protonated molecular ions MH of the DNPH derivatives of formaldehyde (MH = 211), cyclohexanone (MH = 279), octanal (MH = 309), and nonanal (MH = 323). The spectrum of a reference standard for nonanal–DNPH recorded under identical conditions (not shown) contains only two peaks, one large peak at m/e 323 (MH) and a smaller one at m/e 324 (^{14}C isotopic contribution to MH).

included in most experiments (19–21). The sampling performance of the DNPH-coated C_{18} cartridge has been described in detail elsewhere (19–21) for many carbonyls including those relevant to this study.

Cartridge samples were eluted with HPLC-grade acetonitrile and were analyzed by liquid chromatography with isocratic elution and single wavelength ultraviolet detection, liquid chromatography with gradient elution and diode array UV–visible detection, and chemical ionization mass spectrometry (19–21). Spectra of carbonyl DNPH derivatives (290–600 nm) were recorded with a diode array detector (19, 21). We operated the mass spectrometer in the chemical ionization (CI) mode with methane as the reagent gas (24). An example of mass spectrum is given in Figure 2 for a sample collected in one of the 1-decene–ozone–cyclohexane experiments. Quantitative analysis involved the use of external reference standards synthesized in our laboratory (19–21).

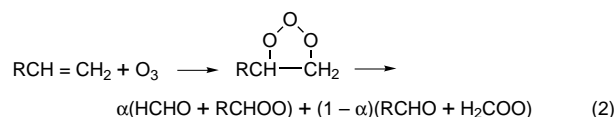
Attempts to synthesize the DNPH derivatives of β -hydroxycarbonyls RCHOHCHO yielded the DNPH derivatives of the corresponding α -dicarbonyls RCOCHO (19). Thus, β -hydroxycarbonyls and α -dicarbonyls could not be resolved if formed together as reaction products. The α -dicarbonyl 2-oxoheptanal, for which no standard is available, was tentatively identified in the ozone–1-octene experiments on the basis of the retention time, 290–600 nm absorption spectrum, and 430/360 nm absorbance ratio of its DNPH derivative. These parameters were consistent with those for DNPH derivatives of other α -dicarbonyls for which standards have been prepared and characterized in previous work (19). The response factor was estimated (uncertainty ca. $\pm 20\%$) using response factor versus retention time data for other α -dicarbonyls (19).

Results and Discussion

Ozone–Alkene Reaction. Carbonyl products identified in the ozone–alkene–cyclohexane experiments (Table 1) were formaldehyde, heptanal, hexanal, and tentatively 2-oxoheptanal from 1-octene; formaldehyde, nonanal, and octanal from 1-decene; pentanal from cyclohexene; and cyclohexanone (a product of the OH–cyclohexane reaction)

from all three alkenes. The formation of OH in the reaction of ozone with 1-octene has been reported previously (13). The formation of OH from 1-decene has not been documented prior to this work. The formation of OH from cyclohexene was first proposed by Hatakeyama et al. (25) to account for some of the carbonyl products identified in ozone–cyclohexene experiments carried out without OH scavenger. The yield of OH produced in the cyclohexene–ozone reaction has been recently measured (26).

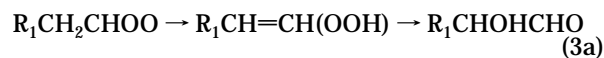
Also listed in Table 1 are carbonyl formation yields, calculated as carbonyl formed, ppb/reacted ozone, ppb, i.e., assuming a 1:1 stoichiometry for the ozone–alkene reaction (14, 27, 28). Carbonyl formation yields for the 1-alkenes were 0.949 ± 0.037 (one standard deviation) for (formaldehyde + heptanal) from 1-octene (which compares to 1.05 ± 0.09 in ref 13) and 1.021 ± 0.018 for (formaldehyde + nonanal) from 1-decene. These yields are close to the value of 1.0 that is consistent with the presently believed mechanism for the ozone–alkene reaction (refs 7, 8, and 14 and references cited therein). This mechanism involves electrophilic addition of ozone followed by decomposition of the 1,2,3-trioxolane adduct into two carbonyls and two biradicals:



Yields of primary carbonyls for 1-octene and 1-decene are comparable to those recently reported for lower molecular weight 1-alkenes in studies involving sufficient alkane added to scavenge OH (13, 27, 28). Thus, data for carbonyl formation yields for 1-alkenes from propene to 1-decene contribute supporting evidence for the simple reaction mechanism summarized by reaction 2.

From the primary carbonyl yields given in Table 1, the coefficient α in reaction 2 is 0.502 ± 0.036 for 1-octene and 0.518 ± 0.017 for 1-decene, consistent with ca. 50:50 formation yields for the biradicals H_2COO and RCHOO in reaction 2.

Carbonyls other than the primary carbonyls formaldehyde, heptanal, and nonanal were observed to form in low yields: hexanal and 2-oxoheptanal from 1-octene, and octanal from 1-decene. Pathways accounting for α -dicarbonyls including 2-oxoheptanal (yield ca. 0.05) have been discussed previously (28). The structural homologue 2-oxononanal [$\text{CH}_3(\text{CH}_2)_6\text{COCHO}$] was not detected in the 1-decene experiments (estimated yield ≤ 0.05). Hexanal and octanal may form from the biradicals RCHOO via the biradical \rightarrow unsaturated hydroperoxide \rightarrow hydroxycarbonyl \rightarrow α -hydroxyalkyl radical sequence, followed by α -hydroxyalkyl + $\text{O}_2 \rightarrow \text{HO}_2$ + carbonyl (14, 27, 28):



where $\text{R}_1 = \text{CH}_3(\text{CH}_2)_4$ for 1-octene and $\text{R}_1 = \text{CH}_3(\text{CH}_2)_6$ for 1-decene. Dividing the measured formation yields of hexanal and octanal by those of formaldehyde, taken to also be the formation yields of the RCHOO biradicals according to reaction 2, gives $\text{CH}_3(\text{CH}_2)_5\text{CHOO} \rightarrow 0.202 \pm$

TABLE 1

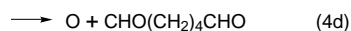
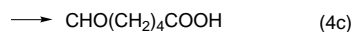
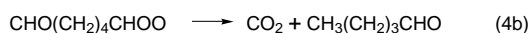
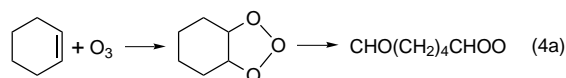
Carbonyl Products of the Ozone–Alkene Reaction

	exp 1	exp 2	exp 3	exp 4	carbonyl yields ^a
		1-Octene			
initial alkene, ppm	1.7	1.6	2.0	8.0	
initial ozone, ppb	170	143	76	422	
carbonyl products, ppb					
formaldehyde	76.1 ± 1.4 ^b	64.1	36.8	216.7	0.476 ± 0.029
hexanal	16.9 ± 4.8	10.2	8.2	43.3	0.096 ± 0.016
heptanal	78.5 ± 0.8	63.0	35.9	212.9	0.473 ± 0.023
cyclohexanone	6.6 ± 0.2	4.1	2.2	12.5	0.032 ± 0.005
2-oxoheptanal ^c	7.8 ± 1.6	6.6	3.5	19.4	0.046 ± 0.002
		1-Decene			
initial alkene, ppm	1.0	1.8	2.0	2.0	
initial ozone, ppb	86	176	98	100	
carbonyl products, ppb					
formaldehyde	41.8	89.9 ± 1.4 ^b	53.6	56.3	0.529 ± 0.014
octanal	3.4	5.7 ± 0.6	3.8	3.7	0.037 ± 0.005
nonanal	38.9	83.6 ± 3.1	46.7	55.8	0.492 ± 0.012
cyclohexanone	1.8	3.9 ± 0.1	2.7	3.5	0.026 ± 0.004
		Cyclohexene			
initial alkene, ppm	1.0	1.0			
initial ozone, ppb	95	92			
carbonyl products, ppb					
pentanal	14.5 ± 1.2 ^b	14.6 ± 0.8 ^b			0.156 ± 0.004
cyclohexanone	5.4 ± 0.4	4.4 ± 0.3			0.053 ± 0.007

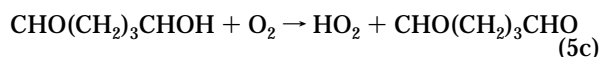
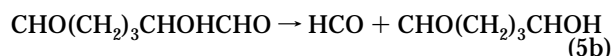
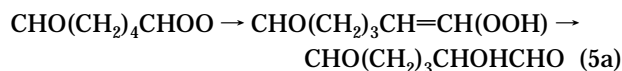
^a Carbonyl formed, ppb/ozone consumed, ppb; average ± one standard deviation. ^b Mean ± 1 SD of data for colocated samples. ^c Tentative identification and estimated concentrations, see text.

0.036CH₃(CH₂)₄CHO for 1-octene and CH₃(CH₂)₇CHOO → 0.070 ± 0.010CH₃(CH₂)₆CHO for 1-decene, indicating, consistent with data for lower molecular weight 1-alkenes (27, 28), that reactions 3a–3c account for ca. 10–20% of the total reactions of the biradicals RCHOO.

The yield of pentanal from cyclohexene, 0.156 ± 0.004, compares to that of 0.17 reported by Hatakeyama et al. for the ozone–cyclohexene reaction studied without scavenging OH (25). The formation of pentanal from cyclohexene, butanal from cyclopentene (13, 28, 29), and 2-hexanone from 1-methylcyclohexene (28) is consistent with the addition of ozone followed by the loss of CO₂ from the biradical (25):



The oxoacid 6-oxohexanoic acid, which forms by rearrangement of the biradical in reaction 4c, has been identified in earlier work (25, 30) and was tentatively identified in this study by chemical ionization mass spectrometry. Vapor pressure considerations together with recent experimental work on aerosol formation from ozone–cyclohexene–cyclohexane mixtures in air (12) indicate that a large fraction of this oxoacid may condense as aerosol under the conditions of this study. Not observed to form in our experiments were adipaldehyde, which may form reaction in 4d, and glutaraldehyde (estimated yield ≤ 1–2%, see the following section), which may form via the biradical → unsaturated peroxide → hydroxycarbonyl sequence analogous to reactions 3a–3c for 1-octene and 1-decene:



Our yield for pentanal from cyclohexene was only ca. 0.16; comparably low carbonyl formation yields have been reported for the reaction of ozone with the cyclic olefins cyclopentene and 1-methylcyclohexene (13, 28, 29). Thus, even when taking aerosol formation into account, a substantial fraction of the products of the ozone–cyclic olefin reaction is not accounted for. Using our measured yield for pentanal, the OH yield of 0.68 (uncertain by a factor of ca. 1.5) from ref 26 and assuming that OH does not form along with pentanal in reaction 4b, the reaction of ozone with cyclohexene can be summarized by the following: O₃ + cyclohexene → 0.16(CO₂ + pentanal) + 0.68(OH + other gas phase products) + β(aerosol products), where β = 0.05–0.2 from recent literature data (4, 12, 25). More information is clearly needed regarding the gas-phase products of the ozone–cyclohexene reaction.

Minor and Unidentified Carbonyls. Unidentified carbonyls observed to form in the ozone–alkene–cyclohexane experiments were as follows: from 1-octene, none; from 1-decene, one minor product; from cyclohexene, two products, one minor and the other more abundant. Retention and absorption parameters for these products are listed in Table 2. These parameters may be useful for identification in future work using retention–structure and absorption–structure relationships (19). The less abundant of the two unidentified carbonyls in the cyclohexene experiments had retention and absorption parameters that matched reasonably well those of the mono-DNPH derivative of glutaraldehyde. Its concentrations were estimated

TABLE 2

Summary of Data for Unidentified Carbonyls

Alkene–Ozone–Cyclohexane Experiments				
carbonyl DNPH derivative				
alkene	retention time ^a	absorption maximum, nm ^b	430/360 nm absorbance ratios ^b	peak height ratios ^c
1-decene	5.0	363	0.26	0.036
cyclohexene	4.7 ^d	361	0.31	0.071
	8.2	360	0.22	0.20

Alkene–NO–Sunlight Experiments				
carbonyl DNPH derivative				
	retention time ^a	430/360 nm absorbance ratios ^b	peak height ratios ^c	
			before crossover	after crossover
1-octene	1.18	0.26	0.065	0.034
	2.33	0.19	<0.01	0.02
cyclohexene	4.12	0.29	0.67	0.08
	4.89 ^d	0.45	3.2	0.46
	8.77	0.40	2.5	0.07
	17.50	0.73	<0.01	0.03

^a Ratio to that of formaldehyde–DNPH, isocratic elution method.

^b From 290 to 600 nm spectrum recorded with diode array detector, gradient elution method. ^c To that of formaldehyde–DNPH for 1-octene and 1-decene and to that of pentanal–DNPH for cyclohexene. ^d Possibly mono-DNPH derivative of glutaraldehyde, see text.

using the response factor for pentanal–DNPH (which eluted close to the unidentified carbonyl) and corresponded to a yield of ≤ 1 –2%.

In addition to the unidentified carbonyls listed in Table 2, the following carbonyls were observed as minor components: from 1-octene, pentanal (yield = $1.7 \pm 0.2\%$); from 1-decene, acetaldehyde and pentanal (each with a yield of ca. 1%); from cyclohexene, formaldehyde (yield $1.9 \pm 0.8\%$) and butanal (yield = $2.6 \pm 0.3\%$). These carbonyls may be carbonyl impurities; ozone–alkene reaction products of alkene impurities; actual reaction products of 1-octene, 1-decene, and cyclohexene via pathways other than those discussed above; and/or products of the alkene reaction with a small fraction of OH that was not scavenged by cyclohexane.

Alkene–NO Mixtures in Sunlight. Sunlight irradiations of alkene–NO mixtures in air resulted in the conversion of NO to NO₂ and in the formation of carbonyls and, after the NO–NO₂ crossover, of ozone, alkyl nitrates, and peroxyacyl nitrates. Carbonyl concentrations and other relevant data are given in Table 3. The NO–alkene sunlight irradiation experiments lead to 11 carbonyls (+ one unidentified) from 1-octene, 11 carbonyls from 1-decene, and 7 carbonyls (+ four unidentified) from cyclohexene. Major carbonyl products were formaldehyde and heptanal from 1-octene, formaldehyde and nonanal from 1-decene, and pentanal from cyclohexene. Retention and absorption parameters for unidentified carbonyls are listed in Table 2.

Few product studies are available for comparison. For 1-octene and 1-decene, our results are comparable to carbonyl data of Grosjean and McMurry (31) for 1-hexene, of Grosjean (32) for 1-heptene (32), and of Atkinson et al. (33) for C₅–C₈ 1-alkenes (although Atkinson et al. reported only two carbonyl products for each of the C₅–C₈ 1-alkenes, e.g., formaldehyde and heptanal from 1-octene). Paulson and Seinfeld (34) also observed heptanal as a major product from 1-octene; formaldehyde was not measured.

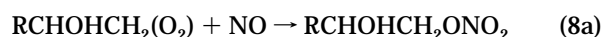
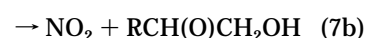
Considerations regarding the mechanism of the alkene–OH reaction indicate that many more carbonyls are predicted to form than was actually observed. Reaction pathways for the reaction of OH with 1-octene, 1-decene, and cyclohexene are described below.

1-Octene–OH and 1-Decene–OH Reaction Pathways.

For the 1-alkenes (1-octene and 1-decene), reaction with OH may involve both addition at the C=C bond and H-atom abstraction from the alkyl substituent CH₂ groups. The abstraction pathway, which has been estimated to account for ca. 15% of the total 1-heptene–OH reaction (33), may be even more important for 1-octene and 1-decene. Nevertheless, addition is the dominant pathway:



The β -hydroxyalkyl radicals formed in reaction 6 react with O₂, and the peroxy radicals thus formed react with NO:



The β -hydroxynitrates formed in reactions 7a and 8a were not identified but may account for ca. 15–17% of the total RO₂ + NO reaction (33, 35). The β -hydroxyalkoxy radicals formed in reactions 7b and 8b may decompose, isomerize, or react with oxygen (33, 36–39). Decomposition leads to (formaldehyde + heptanal) from 1-octene and to (formaldehyde + nonanal) from 1-decene:



where reaction 10c is included to indicate that, unlike CH₂OH, α -hydroxyalkyl radicals that bear large substituents may not react with oxygen exclusively by H-atom abstraction from the OH-bearing carbon (33).

Our observation of formaldehyde and heptanal as major products from 1-octene and of formaldehyde and nonanal as major products from 1-decene indicates that decomposition is important for the β -hydroxyalkoxy radicals RCH(O)CH₂OH and RCHOHCH₂O [R = CH₃(CH₂)₅ and R = CH₃(CH₂)₇]. Competing with decomposition are reaction with oxygen and isomerization (33, 36–39). The corresponding carbonyl products, i.e., β -hydroxycarbonyls and dihydroxycarbonyls, respectively, could not be identified. Thus, the extent of isomerization, which has been shown in recent work to be an important component of the overall alkoxy radical reactions (33, 36–38), could not be assessed in this study.

TABLE 3

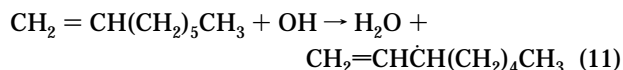
Summary of Data for Alkene—NO Sunlight Irradiation Experiments

1-Octene				
	exp 1	exp 2	exp 3	
initial concentrations				
alkene, ppm	4.0	1.5	2.0	
NO, ppb	840	50	97	
NO ₂ , ppb	0	220	0	
NO–NO ₂ crossover min from start	157	72	42	
NO ₂ max, ppb	630	275	101	
O ₃ max, ppb	8	347	190	
carbonyls, ppb	before crossover	after crossover	before crossover	after crossover
formaldehyde	16.0	257.0	13.9	199.5
acetaldehyde	6.0	45.3	7.6	22.9
propanal	1.6	11.4	2.4	7.3
2-butanone	1.2	6.2	3.0	3.5
butanal	1.4	10.9	2.3	6.0
pentanal	3.2	10.7	2.0	3.8
glyoxal	0.4	7.8	0.0	1.7
hexanal	9.0	195.4	2.1	96.5
heptanal	31.7	481.7	17.7	304.5
octanal	9.2	21.6	0.0	5.6

1-Decene			
	exp 1	exp 2	exp 3
initial concentrations			
alkene, ppm	3.0	4.0	5.5
NO, ppb	170	60	89
NO–NO ₂ crossover min from start	176	143	219
NO ₂ max, ppb	85	30	32
O ₃ max, ppb	8	10	9
carbonyls, ppb	before crossover	before crossover	before crossover
formaldehyde	13.4	40.8	19.4
acetaldehyde	6.2	9.5	5.0
acetone	1.4	4.7	1.6
propanal	1.4	1.5	0.7
2-butanone	1.4	0.8	0.0
butanal	1.2	1.9	1.1
pentanal	1.6	16.9	6.5
hexanal	2.1	21.2	6.7
heptanal	5.1	3.5	2.0
octanal	0.0	7.9	5.4
nonanal	13.1	49.8	24.3

Cyclohexene					
	exp 1		exp 2		
initial concentrations					
alkene, ppm	2.0		4.8		
NO, ppb	380		745		
NO–NO ₂ crossover min from start	84		51		
NO ₂ max, ppb	320		610		
O ₃ max, ppb	260		192		
carbonyls, ppb	before crossover	after crossover	before crossover	after crossover	after crossover
formaldehyde	2.4	11.4	3.0	34.9	28.8
acetaldehyde	10.3	16.6	5.4	33.9	52.8
acetone	1.8	4.5	0.6	7.3	6.7
propanal	2.8	3.5	1.2	5.1	7.5
butanal	2.5	24.8	1.7	49.2	50.0
pentanal	5.2	165.6	7.0	355.7	348.1
C ₄ dicarbonyl	0.0	8.0	0.0	8.0	24.0

The reactions of 1-octene and 1-decene with OH may also involve H-atom abstraction (six pathways for 1-octene and eight pathways for 1-decene), e.g.

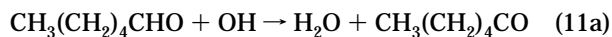


Alkyl radicals formed in reaction 11 and in the other H-atom abstraction pathways may react as discussed above, i.e., $\text{R} + \text{O}_2 \rightarrow \text{RO}_2$, $\text{RO}_2 + \text{NO} \rightarrow (\text{RO} + \text{NO}_2)$ and RONO_2 , followed by RO decomposition, RO isomerization, and RO reaction with oxygen. For 1-octene, the RO decomposition pathways are expected to yield hexanal, pentanal, butanal, propanal, and acetaldehyde, as was indeed observed. However, these carbonyls may also form following OH addition by subsequent reactions of heptanal from 1-octene and of nonanal from 1-decene. Thus, the extent of abstraction in the 1-octene-OH and 1-decene-OH reactions could not be assessed from our experimental data.

Cyclohexene-OH Reaction. The carbonyl products identified (Table 3) gave little information regarding the mechanism of the OH-cyclohexene reaction. Pentanal, the most abundant product observed, forms in the cyclohexene-ozone reaction as discussed earlier. Subsequent reactions of pentanal (photolysis and reaction with OH) lead to butanal, propanal, acetaldehyde, and formaldehyde as was observed.

Adipaldehyde and three C_6 cyclic products (namely, 2-hydroxycyclohexyl nitrate, 2-hydroxycyclohexanone, and 2,4-dihydroxycyclohexanone) are the products expected to form by reaction of OH with cyclohexene according to pathways analogous to those discussed above for the 1-octene-OH and 1-decene-OH addition reactions. Further reactions of adipaldehyde are expected to lead to formaldehyde and to the lower molecular weight α,ω -dialdehyde $\text{CHO}(\text{CH}_2)_n\text{CHO}$, where $n = 0-3$. From vapor pressure considerations, it is likely that most of the adipaldehyde, if formed in our experiments, would condense as aerosol. Adipaldehyde has been identified as an aerosol product of cyclohexene oxidation in previous work (25, 30). The three C_6 polyfunctional oxygenated products predicted to form may also condense as aerosol.

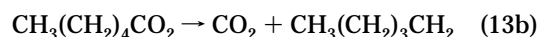
Aldehyde-NO Sunlight Irradiations. Sunlight irradiations of heptanal-NO mixtures were carried out with, as major objectives, the in-situ production of the high molecular weight peroxyacyl nitrate $\text{CH}_3(\text{CH}_2)_5\text{C}(\text{O})\text{OONO}_2$ and the subsequent measurement of its rate of thermal decomposition. Similar experiments were carried out with hexanal to produce $\text{CH}_3(\text{CH}_2)_4\text{C}(\text{O})\text{OONO}_2$, which has not been studied before in the gas phase. All C_1 - C_5 aldehydes formed from hexanal, and all C_1 - C_6 aldehydes formed from heptanal, with the major products being pentanal from hexanal, hexanal from heptanal, and acetaldehyde from both. These aldehydes are expected to form by reaction with OH and by photolysis. For example, the OH-hexanal reaction proceeds as follows:



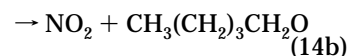
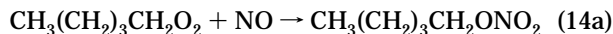
After the NO- NO_2 crossover ($\text{NO}_2 \gg \text{NO}$), the RCO_3 radical reacts with NO_2 to form the peroxyacyl nitrate $\text{RC}(\text{O})\text{OONO}_2$:



Before the NO- NO_2 crossover ($\text{NO} > \text{NO}_2$), the RCO_3 radical reacts with NO, leading to NO_2 , CO_2 , and the *n*-pentyl radical:



followed by $\text{R} + \text{O}_2 \rightarrow \text{RO}_2$ and by $\text{RO}_2 + \text{NO}$ as shown below:



The alkoxy radical formed in reaction 14b may decompose, isomerize, or react with O_2 (33, 36-39). Reaction with O_2 leads to pentanal + HO_2 , decomposition leads to formaldehyde + the *n*-butyl radical, and isomerization leads to products including 4-hydroxypentanal. The *n*-pentyl radical produced in reaction 13b may also form directly by photolysis of hexanal:



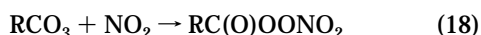
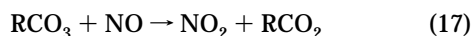
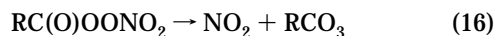
In turn, pentanal reacts with OH and photolyzes, leading to butanal; butanal leads to propanal, propanal to acetaldehyde, and acetaldehyde to formaldehyde.

Our results provide only limited information regarding the relative importance of decomposition, isomerization, and reaction with O_2 for the relevant alkoxy radicals. The observation of pentanal from hexanal and of hexanal from heptanal as products indicates that reaction of the 1-pentoxy and 1-hexoxy radicals with O_2 does occur under the conditions of this study. Decomposition products were observed, but the same carbonyls may also form in subsequent reactions of pentanal and hexanal. The importance of isomerization could not be assessed since hydroxycarbonyl products were not measured. Recent work indicates that the smaller alkoxy radicals $(\text{CH}_3)_2\dot{\text{C}}\text{HO}$ and $(\text{CH}_3)_2\dot{\text{C}}\text{HCH}_2\text{O}$ (for which isomerization is not possible) react predominantly ($\geq 96\%$) with oxygen (40) and that reaction with oxygen is also important for the 1- and 2-butoxy radicals (leading to butanal and 2-methylpropanal, respectively) under conditions similar to those of this study (18).

Alkyl Nitrates and Peroxyacyl Nitrates. Alkyl nitrates observed to form in the alkene-NO and aldehyde-NO sunlight irradiation experiments included *n*-butyl nitrate from cyclohexene, *n*-pentyl nitrate from hexanal, *n*-hexyl nitrate from heptanal, and an unidentified nitrate from 1-octene (retention time ratio to that of PAN ca. 6.1 on the 70 cm column). Methyl, ethyl, and *n*-propyl nitrate were also observed to form, though in smaller amounts, in the experiments with cyclohexene, 1-octene, hexanal, and heptanal. Peroxyacyl nitrates observed to form in the same experiments included PAN, PPN, PnBN, and *n*- $\text{C}_6\text{H}_{13}\text{C}(\text{O})\text{OONO}_2$ from 1-octene; PAN, PnBN, and *n*- $\text{C}_4\text{H}_9\text{C}(\text{O})\text{OONO}_2$ from cyclohexene; PAN, PPN, and *n*- $\text{C}_5\text{H}_{11}\text{C}(\text{O})\text{OONO}_2$ from hexanal; and PAN, PPN, PnBN, and *n*- $\text{C}_6\text{H}_{13}\text{C}(\text{O})\text{OONO}_2$ from heptanal. The relative abundance of the peroxyacyl nitrates was comparable to that of the carbonyls that are their precursors via reactions analogous to those discussed above for hexanal. To focus on OH chemistry, the 1-decene-NO experiments were terminated before or at the NO- NO_2 crossover, and

therefore no peroxyacyl nitrates were observed in these experiments. The peroxyacyl nitrate that may form from 1-decene, $n\text{-C}_8\text{H}_{17}\text{C}(\text{O})\text{OONO}_2$, was tentatively identified in exploratory experiments involving sunlight irradiations of mixtures of NO and nonanal, which is the major product of the 1-decene- O_3 and 1-decene-OH reactions.

Thermal Decomposition of $n\text{-C}_5\text{H}_{11}\text{C}(\text{O})\text{OONO}_2$ and $n\text{-C}_6\text{H}_{13}\text{C}(\text{O})\text{OONO}_2$. Thermal decomposition is a major removal process for peroxyacyl nitrates in the atmosphere (refs 8, 17, and 18 and references cited therein). The thermal decomposition of $n\text{-C}_4\text{H}_9\text{C}(\text{O})\text{OONO}_2$ has been studied previously (18). The thermal decomposition rates of $n\text{-C}_5\text{H}_{11}\text{C}(\text{O})\text{OONO}_2$ and $n\text{-C}_6\text{H}_{13}\text{C}(\text{O})\text{OONO}_2$ were measured at T = ambient and p = 1 atm of air in the presence of excess NO. The relevant reactions are



followed by $\text{RCO}_2 \rightarrow \text{R} + \text{CO}_2$ and subsequent reactions of the alkyl radical R as discussed above.

Under the conditions of our study (excess NO, i.e., $k_{17}[\text{NO}] \gg k_{18}[\text{NO}_2]$), the peroxyacyl nitrate concentration is given by

$$-d(\ln[\text{RCO}_3\text{NO}_2])/dt = k_{16} \ln ([\text{RCO}_3\text{NO}_2]_0/[\text{RCO}_3\text{NO}_2]) = k_{16}t \quad (\text{I})$$

where $[\text{RCO}_3\text{NO}_2]_0$ is the initial peroxyacyl nitrate concentration. The thermal decomposition rates of $n\text{-C}_5\text{H}_{11}\text{C}(\text{O})\text{OONO}_2$ and $n\text{-C}_6\text{H}_{13}\text{C}(\text{O})\text{OONO}_2$ were calculated by plotting the experimental data according to eq I. Examples of these plots are shown in Figure 3 for two experiments, one involving $n\text{-C}_5\text{H}_{11}\text{C}(\text{O})\text{OONO}_2$ synthesized in the liquid phase and the other involving $n\text{-C}_5\text{H}_{11}\text{C}(\text{O})\text{OONO}_2$ prepared in-situ by sunlight irradiation of a mixture of hexanal and NO in air. Least squares linear regression analysis of the data yielded near-zero intercepts, correlation coefficients of $R \geq 0.97$, and slopes, i.e., k_{16} , that are listed in Table 4.

The range of ambient temperatures covered in this study was only ca. 8 K for $n\text{-C}_5\text{H}_{11}\text{C}(\text{O})\text{OONO}_2$ and 4 K for $n\text{-C}_6\text{H}_{13}\text{C}(\text{O})\text{OONO}_2$ and was therefore too narrow to warrant presentation of the results in Arrhenius form. Thermal decomposition rate constants at 298 K, estimated from the data in Table 4, are ca. $1.9 \times 10^{-4} \text{ s}^{-1}$ for $n\text{-C}_5\text{H}_{11}\text{C}(\text{O})\text{OONO}_2$ and ca. $1.0 \times 10^{-4} \text{ s}^{-1}$ for $n\text{-C}_6\text{H}_{13}\text{C}(\text{O})\text{OONO}_2$. These rates compare to those of $3.0 \times 10^{-4} \text{ s}^{-1}$ for PAN (17), $3.4 \times 10^{-4} \text{ s}^{-1}$ for $\text{C}_2\text{H}_5\text{C}(\text{O})\text{OONO}_2$ (17), $3.0 \times 10^{-4} \text{ s}^{-1}$ for $\text{CH}_2=\text{CHC}(\text{O})\text{OONO}_2$ (17), $2.7 \times 10^{-4} \text{ s}^{-1}$ for $n\text{-C}_3\text{H}_7\text{C}(\text{O})\text{OONO}_2$ (41), and $1.8 \times 10^{-4} \text{ s}^{-1}$ for $n\text{-C}_4\text{H}_9\text{C}(\text{O})\text{OONO}_2$ (18) calculated at 298 K from data obtained under the same conditions and using the same measurement protocol. These results suggest that the thermal stability of n -alkyl-substituted peroxyacyl nitrates at ca. 298 K increases with the size of the alkyl substituent. This possible trend should be investigated in future work over a larger range of temperatures relevant to the atmospheric removal of peroxyacyl nitrates by thermal decomposition.

The thermal decomposition of the peroxyacyl nitrates resulted in the formation of carbonyls and organic nitrates. These included, as abundant products, pentanal and n -pentyl nitrate from $n\text{-C}_5\text{H}_{11}\text{C}(\text{O})\text{OONO}_2$ and hexanal and

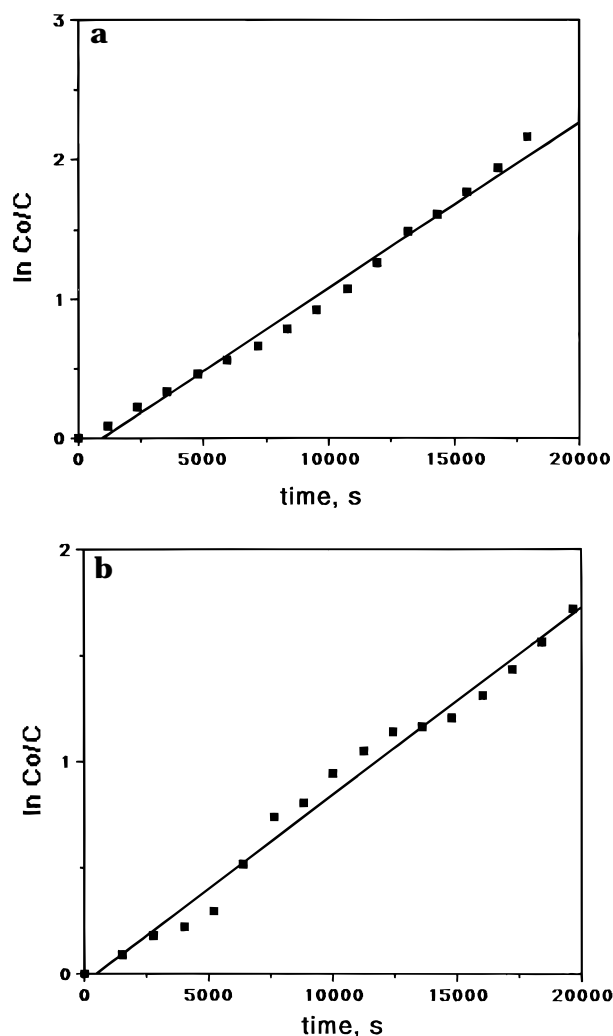


FIGURE 3. Scatter plots of experimental data for thermal decomposition of $n\text{-C}_5\text{H}_{11}\text{C}(\text{O})\text{OONO}_2$ synthesized in the liquid phase (a) and prepared in-situ by sunlight irradiation of hexanal and NO in air (b).

TABLE 4

Summary of Thermal Decomposition Data for $n\text{-C}_5\text{H}_{11}\text{C}(\text{O})\text{OONO}_2$ and $n\text{-C}_6\text{H}_{13}\text{C}(\text{O})\text{OONO}_2$

T , K	slope = thermal decomposition rate, 10^{-4} s^{-1} ^a	intercept ^a	n ^b	R ^c	comments
$n\text{-C}_5\text{H}_{11}\text{C}(\text{O})\text{OONO}_2$					
290.6	0.718 ± 0.016	0.05 ± 0.02	21	0.995	d
293.1	1.13 ± 0.03	0.14 ± 0.04	21	0.995	d
294.3	1.35 ± 0.05	-0.23 ± 0.07	19	0.987	e
295.6	1.71 ± 0.04	-0.27 ± 0.05	22	0.996	e
298.6	2.02 ± 0.04	0.08 ± 0.04	15	0.998	e
$n\text{-C}_6\text{H}_{13}\text{C}(\text{O})\text{OONO}_2$					
291.3	0.611 ± 0.015	0.06 ± 0.02	18	0.995	d
292.4	1.190 ± 0.039	-0.11 ± 0.04	16	0.994	d
294.4	0.753 ± 0.022	0.02 ± 0.03	14	0.995	e
294.9	0.882 ± 0.034	-0.09 ± 0.03	12	0.992	e
295.4	0.884 ± 0.030	-0.04 ± 0.03	17	0.992	e

^a Least squares linear regression of experimental data according to eq I, ± 1 SD. ^b Number of measurements. ^c Correlation coefficient.

^d Peroxyacyl nitrate prepared in-situ by sunlight irradiation of aldehyde-NO mixtures in air. ^e Peroxyacyl nitrate synthesized in the liquid phase.

n -hexyl nitrate from $n\text{-C}_6\text{H}_{13}\text{C}(\text{O})\text{OONO}_2$. These products are consistent with reactions 16 and 17 followed by RCO_2

$\rightarrow R + CO_2$, $R + O_2 \rightarrow RO_2$, and the competing pathways $RO_2 + NO \rightarrow RO + NO_2$ and $RO_2 + NO \rightarrow RONO_2$. Our observation of pentanal and hexanal indicates that subsequent reactions of the pentoxy and hexoxy radicals include reaction with O_2 . Carbonyls expected to result from isomerization could not be identified, and thus the possible importance of isomerization could not be assessed.

Concluding Comments. Atmospheric reactions of 1-octene, 1-decene, and cyclohexene have been studied in laboratory experiments involving alkene- O_3 mixtures in the dark (with sufficient cyclohexane added to scavenge OH) and alkene-NO mixtures in the sunlight. For 1-octene and 1-decene, reaction with ozone leads to the primary carbonyls heptanal from 1-octene, nonanal from 1-decene, and formaldehyde from both. Yields of primary carbonyls were consistent with the simple mechanism: $RCH=CH_2 + O_3 \rightarrow \alpha(HCHO + RCHO) + (1-\alpha) \rightarrow (RCHO + H_2COO)$, where $\alpha + (1-\alpha) = 1.0$ and $\alpha = 0.50$. Carbonyls other than the primary carbonyls were identified and accounted for ca. 10–20% of the subsequent reactions of the biradical $RCHOO$. For cyclohexene, reaction with ozone lead to pentanal (yield ca. 0.16), consistent with loss of CO_2 from the biradical $CHO(CH_2)_4CHOO$.

Sunlight irradiation of alkene-NO mixtures leads to carbonyls, alkyl nitrates, and peroxyacyl nitrates. Reaction mechanisms outlined for the OH-alkene reaction indicate that many more carbonyls and other products may form than were actually observed. The reaction of OH with the 1-alkenes (1-octene and 1-decene) may involve addition and abstraction. The β -hydroxyalkoxy radicals formed via the $OH + RCH=CH_2$ addition pathway and the alkoxy radicals formed in several pathways (including subsequent reactions of the carbonyl products of the OH-alkene reaction) may decompose, isomerize, or react with oxygen. Experimental results provided evidence for addition being the major OH-alkene reaction pathway, for decomposition being important for β -hydroxyalkoxy radicals, and for reaction with O_2 being of some importance for alkoxy radicals. The importance of isomerization for alkoxy and β -hydroxyalkoxy radicals could not be assessed. Data for carbonyl products from hexanal and heptanal in sunlight irradiations of aldehyde-NO mixtures and for carbonyl products of the thermal decomposition of peroxyacyl nitrates also indicated that reaction with O_2 is of some importance for the relevant alkoxy radicals. Carbonyls identified as products gave little information regarding the mechanism of the OH-cyclohexene reaction.

Peroxyacyl nitrates $[RC(O)OONO_2]$ were identified as products from cyclohexene ($R = n-C_4H_9$), hexanal ($R = n-C_5H_{11}$), heptanal and 1-octene ($R = n-C_6H_{13}$). The thermal decomposition rates of $n-C_5H_{11}C(O)OONO_2$ and $n-C_6H_{13}C(O)OONO_2$, which were synthesized in the liquid phase and characterized in a number of tests, were measured in the presence of NO at ambient temperature and $p = 1$ atm of air and were (in units of $10^{-4} s^{-1}$) 0.72–2.02 (290.6–298.6 K) and 0.61–1.19 (291.3–295.4 K), respectively. Comparison of thermal decomposition data with those for lower molecular weight homologues including PAN suggests that the thermal stability of n -alkyl-substituted peroxyacyl nitrates may increase with the size of the alkyl group.

The amount of information obtained in this work varied for each alkene and for each chemistry regime studied. For the 1-alkenes, results for carbonyl products of the ozone reaction may be used to assess the persistence and fate of high molecular weight alkenes in the atmosphere, for

example, using computer kinetic air quality models. More information on carbonyls and other products is needed before realistic attempts can be made to model the multiple reaction pathways that are involved in the reaction of OH with high molecular weight 1-alkenes. For cyclohexene, as in previous work on gas-phase products of cyclic olefins, only limited information was obtained for the ozone reaction and even less for the OH reaction.

With respect to atmospheric persistence, the information on reaction products obtained in this study, together with the relevant kinetic considerations, indicate that the alkenes studied lead to both short-lived and long-lived products. The three alkenes studied react rapidly with ozone and with OH (7, 8, 42). The aldehydes formed as major products react rapidly with OH (8) and are also removed by photolysis. The atmospheric persistence of peroxyacyl nitrates is a function of the NO/ NO_2 ratio. When $NO > NO_2$, peroxyacyl nitrates are removed rapidly due to thermal decomposition. When $NO_2 > NO$, thermal decomposition is no longer important, and our results for $n-C_5H_{11}C(O)OONO_2$ and $n-C_6H_{13}C(O)OONO_2$ suggest that these two compounds are more stable than PAN. However, reaction with OH, which is negligibly slow for PAN, should contribute to the removal of higher molecular weight peroxyacyl nitrates (18). Alkyl nitrates, whose removal involves their slow reaction with OH (8), are expected to be the most persistent among the reaction products of cyclohexene, 1-octene, and 1-decene under atmospheric conditions.

Acknowledgments

This work has been supported in part by the U.S. Environmental Protection Agency Center on Airborne Organics (R-819714-01-0); by National Science Foundation grant ATM-9307603; by the Coordinating Research Council, Inc., Project AQ-1-2; and by internal R&D funds, DGA, Inc., Ventura, CA. Work presented in part as papers ENVR-105 and ENVR-107, 209th National Meeting of the American Chemical Society, Anaheim, CA, April 2–7, 1995.

Literature Cited

- (1) National Research Council. *Ozone and other photochemical oxidants*; National Academy of Sciences: Washington, DC, 1977.
- (2) National Research Council. *Rethinking the ozone problem in urban and regional air pollution*; National Academy Press: Washington, DC, 1991.
- (3) Seinfeld, J. H. *Science* **1989**, *243*, 745–752.
- (4) Grosjean, D.; Seinfeld, J. H. *Atmos. Environ.* **1989**, *23*, 1733–1747.
- (5) Grosjean, D. *Atmos. Environ.* **1992**, *26A*, 953–963.
- (6) Bowman, F. M.; Pilinis, C.; Seinfeld, J. H. *Atmos. Environ.* **1995**, *29*, 579–589.
- (7) Atkinson, R.; Carter, W. P. L. *Chem. Rev.* **1984**, *84*, 437–470.
- (8) Atkinson, R. *J. Phys. Chem. Ref. Data, Monograph 2*, **1994**, 216 pp.
- (9) Grosjean, D.; Van Cauwenberghe, K.; Schmid, J.; Kelley, P. E.; Pitts, J. N., Jr. *Environ. Sci. Technol.* **1978**, *12*, 313–317.
- (10) Grosjean, D.; Williams, E. L., II; Grosjean, E.; Andino, J. M.; Seinfeld, J. H. *Environ. Sci. Technol.* **1993**, *27*, 2754–2758.
- (11) Grosjean, D.; Williams, E. L., II; Seinfeld, J. H. *Environ. Sci. Technol.* **1992**, *26*, 1526–1533.
- (12) Grosjean, D.; Williams, E. L., II; Grosjean, E.; Novakov, T. *Aerosol Sci. Technol.* **1994**, *21*, 306–324.
- (13) Atkinson, R.; Tuazon, E. C.; Aschmann, S. M. *Environ. Sci. Technol.* **1995**, *29*, 1860–1866.
- (14) Grosjean, D.; Grosjean, E.; Williams, E. L., II. *Environ. Sci. Technol.* **1994**, *28*, 186–196.
- (15) Grosjean, D.; Williams, E. L., II; Seinfeld, J. H. *Environ. Sci. Technol.* **1993**, *27*, 830–840.
- (16) Grosjean, D.; Williams, E. L., II; Grosjean, E. *Environ. Sci. Technol.* **1993**, *27*, 110–121.
- (17) Grosjean, D.; Grosjean, E.; Williams, E. L., II. *J. Air Waste Manage. Assoc.* **1994**, *44*, 391–396.

- (18) Grosjean, D.; Grosjean, E.; Williams, E. L., II. *Environ. Sci. Technol.* **1994**, *28*, 1099–1105.
- (19) Grosjean, E.; Grosjean, D. *Int. J. Environ. Anal. Chem.* **1995**, *61*, 47–64.
- (20) Grosjean, E.; Grosjean, D. *Int. J. Environ. Anal. Chem.* **1995**, *61*, 343–360.
- (21) Grosjean, E.; Grosjean, D.; Fraser, M. P.; Cass, G. R. An air quality model evaluation data set for organics. 2. C₁–C₁₄ carbonyls in Los Angeles air. *Environ. Sci. Technol.*, submitted for publication.
- (22) Grosjean, D.; Grosjean, E.; Williams, E. L., II. *Int. J. Chem. Kinetics* **1993**, *25*, 783–794.
- (23) Grosjean, E.; Grosjean, D. *Int. J. Chem. Kinet.* **1994**, *26*, 1185–1191.
- (24) Grosjean, D. *Anal. Chem.* **1983**, *55*, 2436–2439.
- (25) Hatakeyama, S.; Tanonaka, T.; Weng, J.; Bandow, H.; Takagi, H.; Akimoto, H. *Environ. Sci. Technol.* **1985**, *19*, 935–942.
- (26) Atkinson, R.; Aschmann, S. M. *Environ. Sci. Technol.* **1993**, *27*, 1357–1363.
- (27) Grosjean, E.; de Andrade, J. B.; Grosjean, D. Carbonyl products of the gas phase reaction of ozone with simple alkenes. *Environ. Sci. Technol.*, in press.
- (28) Grosjean, E.; Grosjean, D. Carbonyl products of the gas phase reaction of ozone with C₅–C₇ alkenes. *Environ. Sci. Technol.*, in press.
- (29) Hatakeyama, S.; Ohno, M.; Weng, J.; Tagaki, H.; Akimoto, H. *Environ. Sci. Technol.* **1987**, *21*, 52–57.
- (30) Grosjean, D.; Friedlander, S. K. Formation of organic aerosols from cyclic olefins and diolefins. In *The Character and Origins of Smog Aerosols*; Hidy, G. M., et al., Eds.; Wiley: New York, 1979; pp 435–473.
- (31) Grosjean, D.; McMurry, P. H. Secondary organic aerosol formation: homogeneous and heterogeneous chemical pathways. Report PB-82-262262; National Technical Information Service: Springfield, VA, 1982.
- (32) Grosjean, D. *Sci. Total Environ.* **1984**, *37*, 195–211.
- (33) Atkinson, R.; Tuazon, E. C.; Aschmann, S. M. *Environ. Sci. Technol.* **1995**, *29*, 1674–1680.
- (34) Paulson, S. E.; Seinfeld, J. H. *Environ. Sci. Technol.* **1992**, *26*, 1165–1173.
- (35) Atkinson, R.; Carter, W. P. L. *J. Atmos. Chem.* **1989**, *8*, 165–173.
- (36) Eberhard, J.; Müller, C.; Stocker, D. W.; Kerr, J. A. *Environ. Sci. Technol.* **1995**, *29*, 232–241.
- (37) Atkinson, R.; Aschmann, S. M. *Environ. Sci. Technol.* **1995**, *29*, 528–536.
- (38) Atkinson, R.; Aschmann, S. M. *Int. J. Chem. Kinet.* **1995**, *27*, 261–275.
- (39) Atkinson, R.; Carter, W. P. L. *J. Atmos. Chem.* **1991**, *13*, 195–210.
- (40) Grosjean, D.; Grosjean, E.; Williams, E. L., II. *Environ. Sci. Technol.* **1994**, *28*, 167–172.
- (41) Grosjean, D.; Grosjean, E.; Williams, E. L., II. *Res. Chem. Intermed.* **1994**, *20*, 447–461.
- (42) Grosjean, E.; Grosjean, D. *Int. J. Chem. Kinet.* **1995**, *27*, 1045–1054.

Received for review August 10, 1995. Revised manuscript received November 8, 1995. Accepted November 8, 1995.[®]
 ES950592Z

[®] Abstract published in *Advance ACS Abstracts*, February 1, 1996.